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(54) **Photostereolithographic process.**

- (57) A method of generating three-dimensional objects comprising applying light of wavelength 450-550 nm by a stereolithographic technique to a photopolymerisable resin composition comprising :
- (a) a compound having at least one polymerisable unsaturated bond per molecule and a free radical photoinitiator, and/or
  - (b) a compound capable of cationic polymerisation and a cationic photoinitiator,
- said photopolymerisable resin composition also containing a compound of which the wavelength of maximum absorption is in the range 400-600 nm.

**EP 0 535 828 A1**

This invention relates to a method of forming a three-dimensional moulding from a photopolymerisable resin having high sensitivity to active radiation. In particular, it relates to a photostereolithographic technique using a resin composition from which mouldings having high dimensional accuracy can be formed because of the improved cure depth of the liquid photocurable resin composition when subjected to selective exposure using a laser beam optical system.

A stereolithographic technique is known whereby an amount of a liquid photocurable resin composition corresponding to one layer or slice of a three-dimensional article to be formed is supplied to a container located on a movable platform and irradiated with a programmed laser beam so as to form a solidified layer of cured resin. The platform is then lowered, further unpolymerised resin composition is supplied on top of the cured layer and the process is repeated until the complete object is constructed, slice by slice, from the bottom to the top. The formed article may then be subjected to a post-cure to minimise residual unpolymerised material. The technique allows the rapid construction of solid, complex shaped, three-dimensional objects without the need for expensive tooling equipment or moulds, especially objects containing voids or having irregular shapes.

In the aforementioned technique, it is known to use a UV-curable resin composition and a helium-cadmium laser as a source of ultraviolet radiation. For reasons of safety, more economical equipment and improved power output, it is also known to use visible light argon-ion lasers but, in visible light cured systems, there has been an accuracy problem related to the cure depth. In this connection, "cure depth" means the depth (thickness) of cure obtained when a photocurable resin composition is irradiated with light.

In said photomoulding technique, the production of three-dimensional shapes with the desired accuracy has been a problem because of the need to control the cure depth so as to be of the same order as the step width, that is to say the thickness of a single layer of the layers which make up the three-dimensional shape. Since the step width is generally about 100 microns ( $\mu\text{m}$ ), the cure depth should not exceed 500 microns (0.5 mm) and should preferably be 100 microns or less but, generally speaking, a photoradical polymerisation initiator or a photocationic polymerisation initiator for the visible light region has a small extinction coefficient and limited solubility in a resin compared with corresponding initiators for ultraviolet radiation resulting in a cure depth of 1.0 mm or more with consequent severe deterioration in the dimensional accuracy of the moulding.

It is an object of the invention to solve the above mentioned problem by providing a three-dimensionally mouldable photocurable resin composition having a cure depth of 0.5 mm or less when exposed to visible light.

It has now been found that the cure depth of a photocurable resin composition can be controlled by dispersing or dissolving therein a compound having maximum absorption in the wavelength range 400-600 nm, the cure of the resin composition being controllable to a depth of 0.5 mm or less when irradiated by light having a wavelength in the range 450-550 nm.

Accordingly, the present invention provides a method of generating three-dimensional objects comprising applying light of wavelength 450-550 nm by a stereolithographic technique to a photopolymerisable resin composition comprising:

(a) a compound having at least one polymerisable unsaturated bond per molecule and a free radical photoinitiator, and/or

(b) a compound capable of cationic polymerisation and a cationic photoinitiator,

said photopolymerisable resin composition also containing a compound of which the wavelength of maximum absorption is in the range 400-600 nm.

There is no particular restriction on the type of compound (hereinafter referred to as a dye) having a wavelength of maximum absorption ( $\lambda_{\text{max}}$ ) in the range 400-600 nm so long as it is sufficiently soluble in the photocurable resin composition and it may be a dye of, for example, the xanthene, anthraquinone or azo series.

Suitable examples of dyes include xanthene dyes such as 2',7'-dichlorofluorescein, Chromazurol S, Erythrosine B, Methyl Eosine and merbromin, anthraquinone dyes such as Disperse Orange 11, New Clear Fast Red and 1-methylaminoanthraquinone, azo dyes such as Disperse Orange 1, Disperse Orange 3, Disperse Orange 13, Disperse Orange 25, Disperse Red 1, Disperse Red 13, Disperse Yellow 3 and the like.

Dyes capable of acting as photosensitisers are preferred because of their advantageous effect on the photopolymerisation.

As examples of compounds having at least one polymerisable unsaturated bond per molecule, there may be mentioned the following classes of ethylenically unsaturated compounds:

(1) Unsaturated polyesters such as may be obtained by direct esterification of an unsaturated polycarboxylic acid or anhydride thereof, a saturated polycarboxylic acid or anhydride thereof and a polyol.

Suitable unsaturated acids or anhydrides include maleic anhydride, fumaric acid, citraconic acid and itaconic acid.

Suitable saturated acids or anhydrides include phthalic anhydride, isophthalic acid, terephthalic acid, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, succinic acid, adipic acid, azelaic acid, sebacic acid, tetrachlorophthalic anhydride and endomethylene tetrahydrophthalic anhydride.

Suitable polyols include ethylene glycol, propylene glycol, 1,4-butanediol, 1,3-butanediol, 2,3-butanediol, diethylene glycol, dipropylene glycol, triethylene glycol, 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, hydrogenated bisphenol A, glycerol, trimethylolpropane monoallyl ether and glycerol monoallyl ether.

(2) Polyester acrylates such as may be obtained by direct esterification of a polyol, a polycarboxylic acid or anhydride thereof and acrylic acid in the presence of a catalyst.

Suitable polyols include ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, 1,4-butanediol, 1,3-butanediol, 1,6-hexanediol, neopentyl glycol, hydrogenated bisphenol A, glycerol, trimethylolpropane, pentaerythritol and dipentaerythritol.

Suitable polybasic acids or anhydrides include phthalic anhydride, isophthalic acid, terephthalic acid, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, succinic acid, adipic acid, azelaic acid and sebacic acid.

(3) Urethane acrylates such as may be obtained by reaction of an unsaturated alcohol such as 2-hydroxyethyl acrylate, a polyester or polyether polyol and a diisocyanate.

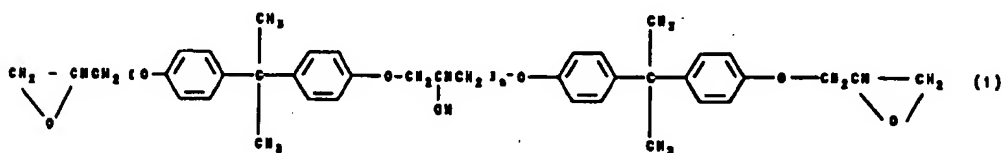
Suitable polyester polyols include esterification products of the polyols and polybasic acids mentioned in (2) above as well as polycaprolactone polyols.

Suitable polyether polyols include polyethylene glycol, polypropylene glycol and polytetramethylene glycol.

Suitable diisocyanates include toluene diisocyanate, 4,4'-diphenylmethane diisocyanate, hexamethylene diisocyanate and isophorone diisocyanate.

(4) Epoxy acrylates such as reaction products of bisphenol diglycidyl ethers, diglycidyl esters or alicyclic epoxy compounds having at least two epoxy groups per molecule with acrylic acid.

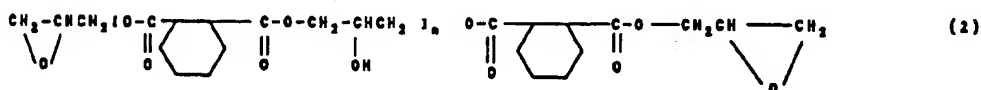
Suitable bisphenol diglycidyl ethers include compounds of the formula:



where n is an integer from 0 to 12.

Examples include the Shell products Epikote 827, Epikote 828 and Epikote 1001.

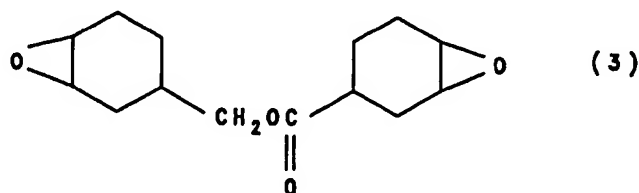
Suitable diglycidyl esters include compounds of the formula:



where n is as defined above.

Examples include the Ciba-Geigy products Araldite CY-175 and Araldite CY-176.

Suitable alicyclic epoxy compounds include 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexane carboxylate having the formula:



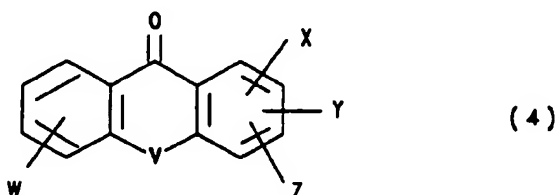
(5) Unsaturated acrylate series compounds such as may be obtained by reaction of an unsaturated spir-o-acetal, an unsaturated alcohol such as 2-hydroxyethyl acrylate and a saturated polyol or polyester polyol with or without modification. These unsaturated compounds comprise oligomers or polymers having at

least one, preferably two or more unsaturated groups per molecule as the main components.

As examples of free radical generating photoinitiators to be included in the photopolymerisable resin composition, there may be mentioned  $\alpha$ -ketocarbonyl compounds, thioxanthone compounds, anthraquinone compounds, acyl phosphine oxide compounds, onium salts and the like.

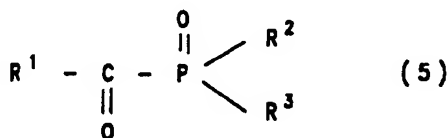
Suitable  $\alpha$ -ketocarbonyl compounds include  $\alpha$ -diketones,  $\alpha$ -ketoaldehydes,  $\alpha$ -ketocarboxylic acids,  $\alpha$ -ketocarboxylates and the like. Examples of  $\alpha$ -diketones include diacetyl, 2,3-pentanedione, 2,3-hexanedione, benzil, 4,4'-dimethoxybenzil, 4,4'-diethoxybenzil, 4,4'-dihydroxybenzil, 4,4'-dichlorobenzil, 4-nitrobenzil,  $\alpha$ -naphthil,  $\beta$ -naphthil, camphorquinone, 1,2-cyclohexanedione and the like. Examples of  $\alpha$ -ketoaldehydes include methylglyoxal, phenylglyoxal and the like. Examples of  $\alpha$ -ketocarboxylic acids and  $\alpha$ -ketocarboxylates include pyruvic acid, benzoylformic acid, phenylpyruvic acid, methyl pyruvate, ethyl benzoylformate, methyl phenylpyruvate, butyl phenylpyruvate and the like. The preferred  $\alpha$ -ketocarbonyl compounds are  $\alpha$ -diketones for stability reasons, the preferred  $\alpha$ -diketones being diacetyl, benzil and camphorquinone.

Suitable xanthone or anthraquinone compounds may be represented by the general formula:



wherein V represents S or CO and each of X, Y, Z and W, independently, represents hydrogen,  $C_1$ - $C_{12}$ -alkyl which may optionally be substituted by hydroxy and/or halogen,  $C_1$ - $C_6$ -alkoxy, benzyloxy, allyloxy,  $C_1$ - $C_6$ -acyloxy which may optionally contain an unsaturated double bond,  $C_1$ - $C_6$ -alkoxycarbonyl which may optionally be substituted by hydroxy and/or halogen, glycidylloxycarbonyl, allyloxycarbonyl, vinyloxycarbonyl, cyclohexyl, phenyl or phenoxy.

Suitable acylphosphine oxide compounds may be represented by the general formula:



wherein  $R^1$  represents optionally substituted phenyl, for example chlorophenyl, methylphenyl and the like, and each of  $R^2$  and  $R^3$ , independently, represents  $C_1$ - $C_{12}$ -alkyl,  $C_1$ - $C_{12}$ -alkoxy or optionally substituted phenyl, for example chlorophenyl, methylphenyl and the like.

Suitable onium salts include the double salts represented by the general formula:



wherein  $Z^1$  represents S, Se, Te, P, As, Sb, Bi, O, halogen (especially I, Br or Cl) or N=N, R represents one or more organic groups which may be the same or different, a represents the sum of the bonds provided by the terminal carbon atoms of said organic groups, c represents the sum of the valences of R and  $Z^1$  (but is the difference if the valence of  $Z^1$  is negative), M represents a metal or metalloid which is the central atom of a halogenated complex and is such as B, P, As, Sb, Fe, Sn, Bi, Al, Ca, In, Ti, Zn, Sc, V, Cr, Mn, Co and the like,  $X^1$  represents a halogen atom, b represents the number of halogen atoms in the halogenated complex ion and c represents the net charge of the halogenated complex ion.

Specific examples of the onion  $MX^1_b$  in the above formula include tetrafluoroborate ( $BF_4$ )<sup>-</sup>, hexafluorophosphate ( $PF_6$ )<sup>-</sup>, hexafluoroantimonate ( $SbF_6$ )<sup>-</sup>, hexafluoroarsenate ( $AsF_6$ )<sup>-</sup>, hexachloroantimonate ( $AsCl_6$ )<sup>-</sup> and the like.

Additionally, onions represented by the general formula  $MX^1_b(OH)^-$  may also be present. Examples of other useful onions include perchlorate ( $ClO_4$ )<sup>-</sup>, trifluoromethylsulphonate ( $CF_3SO_3$ )<sup>-</sup>, fluorosulphonate ( $FSO_3$ )<sup>-</sup>, toluenesulphonate, trinitrobenzenesulphonate and the like.

Of these onium salts, it is particularly effective to use aromatic onium salts as the cationic photoinitiator, and the halonium salt described in Japanese Patent Disclosures 50-151996, 50-158680 etc., the Group VIA

aromatic onium salt described in Japanese Patent Disclosures 50-151997, 52-80899, 56-55420 and 55-125105, the Group VA onium salt described in Japanese Patent Disclosure 50-168698 etc., the oxosulphonium salt described in Japanese Patent Disclosures 56-8428, 56-149402, 57-192429 etc., the thiapyrilium salt described in Japanese Patent Disclosure 49-17040 etc., are especially preferred. Iron-arene complex and aluminium complexes with silicon compounds may also be mentioned as initiators.

The efficiency of these free radical photoinitiators may be improved by combining them with amines.

Amines which may be incorporated in the photocurable resin composition include aliphatic, alicyclic and aromatic amines and they may be primary secondary or tertiary amines. It is preferred to use aromatic amines, especially the tertiary amines.

Examples of specific amines include aliphatic amines such as triethylamine, tripropylamine, tributylamine, tripentylamine, trihexylamine, trioctylamine, diethylamine, dipropylamine, dibutylamine, dihexylamine, butylamine, hexylamine, octylamine, decylamine, dodecylamine and the like, alicyclic amines such as tricyclohexylamine, dicyclohexylamine, cyclohexylamine and the like and aromatic amines such as aniline, toluidine, xylidine, phenylene diamine, N,N-dimethylaniline, N,N-diethylaniline, N,N-di(β-hydroxyethyl) aniline, N,N-dimethyltoluidine, N,N-diethyltoluidine, N,N-dimethylanisidine, N,N-diethylanisidine, N,N-dimethyl-t-butylaniline, N,N-diethyl-t-butylaniline, N,N-dimethyl-p-chloroaniline, diphenylamine, N,N-bis(β-hydroxyethyl)-p-toluidine, 4-dimethylaminobenzoic acid, methyl 4-dimethylaminobenzoate, 4-dimethylaminobenzaldehyde, 4-diethylaminobenzoic acid, methyl 4-diethylaminobenzoate, N,N-dimethyl-p-cyanoaniline, N,N-dimethyl-p-bromoaniline and the like.

Preferred amines include aromatic tertiary amines such as N,N-di(β-hydroxyethyl)aniline, N,N-dimethylaniline, N,N-bis(β-hydroxyethyl)-p-toluidine, N,N-dimethyl-p-toluidine, N,N-dimethylaminobenzoic acid, N,N-diethylaminobenzoic acid and the like.

Furthermore, there may be used a free radical photoinitiator system comprising two or more compounds selected from a halogenated compound as represented by 2,4,6-tris(trichloromethyl)-s-triazine and its derivatives, 1,4,5,6,7,7-hexachloro-5-norbornene-2,3-dicarboxylic anhydride and the like, a peroxide as represented by 1,3-di(t-butyldioxycarbonyl)benzene, 3,3',4,4'-tetrakis(t-butyldioxycarbonyl)benzophenone and the like, a photo-oxide as represented by benzophenone, xanthone and the like, an onium salt as represented by iodonium, sulphonium, iron-arene complex, a dye as represented by dyes of the cyanine series, N-phenylglycine, 3,3'-carbonylbis (7-diethylaminocoumarin) and the like and other dyes as represented by dyes of the xanthene series.

The compound capable of cationic polymerisation which may be used in accordance with the invention is a compound which exhibits a polymerisation or crosslinking reaction when irradiated with an energy beam in the presence of a cationic photoinitiator and may comprise, for example, one or more of an epoxy compound, a cyclic ether, a lactone, a cyclic acetal, a cyclic thioether, a spiro-orthoester, a vinyl compound and the like. Of the compounds capable of cationic polymerisation, known aromatic, alicyclic or aliphatic epoxy compounds having at least two epoxy groups per molecule are preferred.

As preferred examples of epoxy compounds there may be mentioned polyglycidyl ethers of polyphenols having at least one aromatic ring or of the corresponding alkylene oxide adducts. More specific examples include novolak epoxy compounds and glycidyl ethers obtained by the reaction of bisphenol A, bisphenol F or their alkylene oxide adducts with epichlorohydrin.

As preferred examples of alicyclic epoxy compounds, there may be mentioned polyglycidyl ethers of polyols having at least one alicyclic ring or cyclohexene oxide or cyclopentene oxide containing compounds obtained by epoxidation of a cyclohexene or cyclopentene ring containing compound using a suitable oxidant such as hydrogen peroxide, a peracid and the like. As specific examples of alicyclic epoxy compounds, there may be mentioned the diglycidyl ether of hydrogenated bisphenol A, 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexane carboxylate, 2-(3,4-epoxycyclohexyl-5,5-spiro-3,4-epoxy)cyclohexane-m-dioxane, bis(3,4-epoxycyclohexylmethyl) adipate, vinylcyclohexene dioxide, 4-vinylepoxycyclohexane, bis(3,4-epoxy-6-methylcyclohexylmethyl) adipate, 3,4-epoxy-6-methylcyclohexane carboxylate, methylenebis(3,4-epoxycyclohexane), dicyclopentadiene diepoxide, di(3,4-epoxycyclohexylmethyl) ether of ethylene glycol, ethylenebis(3,4-epoxycyclohexane carboxylate), dioctyl epoxyhexahydrophthalate, di-2-ethylhexyl epoxyhexahydrophthalate and the like.

As preferred examples of aliphatic epoxy compounds, there may be mentioned polyglycidyl ethers of aliphatic polyols or their alkylene oxide adducts, polyglycidyl esters of aliphatic long chain polybasic acids, homopolymers or copolymers of glycidyl acrylate or methacrylate and the like. As specific examples, there may be mentioned the diglycidyl ether of 1,4-butanediol, the diglycidyl ether of 1,6-hexanediol, the triglycidyl ether of glycerol, the triglycidyl ether of trimethylolpropane, the tetraglycidyl ether of sorbitol, the hexaglycidyl ether of dipentaerythritol, the diglycidyl ether of polyethylene glycol, the diglycidyl ether of polypropylene glycol, diglycidyl ethers of polyether polyols obtained by addition of at least one alkylene oxide to an aliphatic polyol

such as ethylene glycol, propylene glycol, glycerol, and the like, and diglycidyl esters of aliphatic long chain dibasic acids. Furthermore, monoglycidyl ethers of aliphatic higher alcohols, monoglycidyl ethers of phenol, cresol, butylphenol or polyether alcohols obtained by addition of alkylene oxide to these, monoglycidyl esters of higher fatty acids, epoxidised soyabean oil, butyl epoxystearate, octyl epoxystearate, epoxidised linseed oil, epoxidised polybutadiene and the like can also be used.

As examples of cationic polymerisable compounds other than epoxy compounds, there may be mentioned oxetane compounds such as trimethylene oxide, 3,3-dimethyloxacyclobutane, 3,3-bis(chloromethyl)oxacyclobutane and the like, oxolane compounds such as tetrahydrofuran and 2,3-dimethyltetrahydrofuran, cyclic acetal compounds such as trioxane, 1,3-dioxolane and 1,3,6-trioxacyclo-octane, lactones such as  $\beta$ -propiolactone and E-caprolactone, thiirane compounds such as ethylene sulphide and thioepichlorohydrin, thietane compounds such as 1,3-propylene sulphide and 3,3-dimethylthietane, vinyl ethers such as ethylene glycol divinyl ether, alkyl vinyl ethers, 3,4-dihydrofuran-2-methyl 3,4-dihydropyran-2-carboxylate and triethylene glycol divinyl ether, spiro-orthoester compounds obtained by reaction of an epoxy compound with a lactone and ethylenically unsaturated compounds such as vinylcyclohexane, isobutylene, polybutadiene and derivatives thereof. The cationic polymerisable compound may be used singly or in mixtures of two or more such compounds to provide the desired properties.

The most preferred of the cationic polymerisable compounds are the aliphatic epoxy compounds having at least two epoxy groups per molecule because of their reactivity to cationic polymerisation, low viscosity, transparency to visible light, thick curing and low volume shrinkage.

The cationic photoinitiator which may be used in accordance with the invention is a compound capable of releasing a substance to initiate cationic polymerisation when irradiated with an energy beam. Preferred cationic photoinitiators include double salts which are onium salts capable of releasing a Lewis acid when irradiated by an energy beam. These have been described above in the discussion of free radical photoinitiators.

The amount of dye to be incorporated in the photopolymerisable resin composition should be sufficient to ensure that the cure depth of the composition is 0.5 mm or less when exposed to light of wavelength 450-550 nm and is generally not less than 0.01% by weight and not more than 10%, preferably not more than 1%, by weight. Amounts of dye exceeding 10% by weight can have an adverse effect on the properties of the photopolymerisable resin composition whilst amounts less than 0.01% by weight do not generally provide the desired improvement in the accuracy of the cure depth.

The dye may be used singly or as a mixture of two or more dyes and may also be used jointly with a reducing agent having absorption in the visible light region, for example 3,3'-carbonylbis (7-diethylaminocoumarin).

The amount of the free radical and/or cationic photoinitiator to be incorporated in the photopolymerisable resin composition may vary from 1/5 to 1/500 of the amount of polymerisable unsaturated compound and/or cationic polymerisable compound on a weight basis but is preferably in the range from 1/10 to 1/100. If the amount of the free radical and/or cationic photoinitiator is below the lower limit of the above mentioned range, the photosensitisation rate is reduced and the time taken for the composition to cure (to solidify) is extended. On the other hand, if it exceeds the upper limit of the above mentioned range, there is a deterioration in the strength of the film formed from said composition and in its solvent resistance and it becomes of no practical value.

The photopolymerizable resin composition contains the aforementioned free radical and/or cationic photoinitiator but may also contain other polymerisation initiators or additives for the photopolymerisation. Examples of conventional additives include solvents, polymeric binders, thermal polymerisation inhibitors, plasticisers and organic or inorganic fillers which may be used singly or jointly.

Examples of solvents which may be incorporated in the photopolymerisable resin composition include ketones such as methyl ethyl ketone, acetone, cyclohexanone and the like, esters such as ethyl acetate, butyl acetate and the like, aromatic solvents such as toluene, xylene and the like, "Cellosolve" solvents such as methyl "Cellosolve", ethyl "Cellosolve", butyl "Cellosolve" and the like, alcohols such as methanol, ethanol, propanol and the like and ethers such as tetrahydrofuran, dioxane and the like.

Polymeric binders may be used to improve compatibility, film-forming, developing, adhesion, etc., and may be selected to satisfy the particular application. For example, in order to improve development when using an aqueous solvent, copolymers of acrylic (or methacrylic) acid and an alkyl acrylate (or methacrylate), itaconic acid copolymers, partially esterified maleic acid copolymers, modified cellulose acetate having a carboxyl-substituted side chain, poly(ethylene oxide), poly(vinylpyrrolidone) and the like are useful.

In order to improve film strength and adhesion, polyamides and polyethers derived from the diglycidyl ether of bisphenol A are useful.

Thermal polymerisation inhibitors which may be used include hydroquinone, p-methoxyphenol, pyrogallol, catechol, 2,6-di-t-butyl-p-cresol,  $\beta$ -naphthol and the like.

Useful plasticisers include dialkyl esters of phthalic acid such as dioctyl phthalate, didodecyl phthalate,

dibutyl phthalate and the like and dialkyl esters of aliphatic dibasic acids such as dioctyl adipate, dibutyl adipate, dibutyl sebacate and the like.

Examples of organic fillers include polymethacrylate and nylon beads and fibre reinforcement comprising fibres of carbon, aramids, nylon and the like.

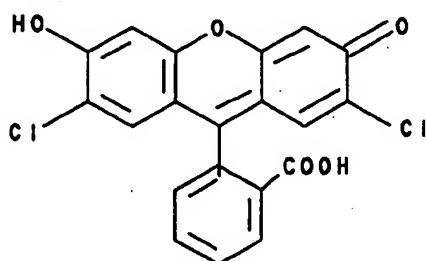
Examples of inorganic fillers include calcium carbonate, calcium silicate, titanium oxide, antimony trioxide, aluminium hydroxide, talc, clay, alumina, calcium hydroxide, magnesium carbonate and the like and fibres derived therefrom.

Suitable light sources for the curing operation include lasers such as argon lasers, helium-cadmium lasers, krypton lasers and the like and also conventional light sources for generating ultraviolet radiation or visible light such as extra high pressure mercury lamps, high pressure mercury lamps, medium pressure mercury lamps, metal halide lamps, xenon lamps, tungsten lamps and the like.

The invention is illustrated but not limited by the following Examples in which all parts are by weight.

### Example 1

A mixture of the diacrylate of ethylene oxide modified bisphenol A (hereinafter described as Monomer I) and isobornyl acrylate (hereinafter described as Monomer II) was used as the ethylenically unsaturated compound. The free radical photoinitiator was camphorquinone (hereinafter described as Initiator I) and the sensitizer was N,N-diethylaminoethyl methacrylate (hereinafter described as Sensitizer I). The dye used was 2',7'-dichlorofluorescein having the formula:



50 parts of Monomer I, 47 parts of Monomer II, 1 part of Initiator I, 1 part of Sensitizer I and 1 part of the dye were thoroughly mixed.

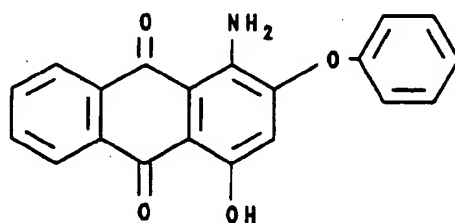
The maximum absorption wavelength ( $\lambda_{\text{max}}$ ) of the photopolymerisable resin composition was determined and the figure (509 nm) shown in Table 2 was obtained. Then, the resin composition was filled into a moulding space hollowed out of the centre of 10 mm thick silicone rubber and was covered by black chloroprene rubber (1 mm thick) having a hole (approx 1 mm<sup>2</sup>) at its centre. The amount of resin composition was adjusted so that its upper level corresponded with the upper level of the chloroprene rubber.

A halogen lamp was then installed at a distance of approximately 5 mm from the aforementioned surface of the hole in the chloroprene rubber and radiation was applied for 1 minute.

After irradiation, the chloroprene rubber was peeled off and the thickness of the photocurable resin adhering to the central hole of said chloroprene rubber because of polymerisation was measured, the cured film thickness being described hereinafter as the cure depth.

### Example 2

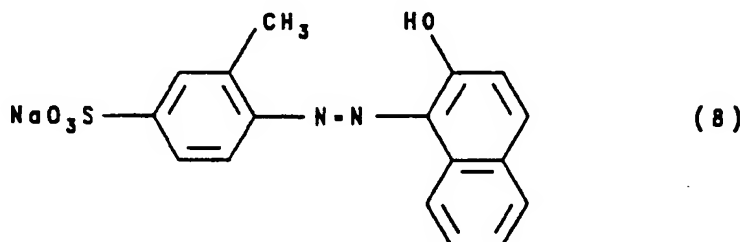
As for Example 1 except that the dye of Formula 6 was replaced by the dye of the formula:



This dye is DISPERSOL Red B-2B available from Imperial Chemical Industries PLC.

### Example 3

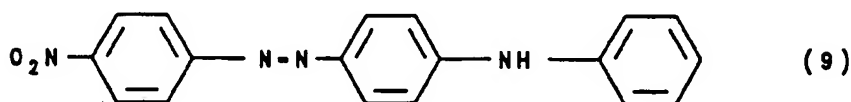
As for Example 1 except that the dye of Formula 6 was replaced by the dye of the formula:



This dye is C.I. Acid Orange 8.

### Example 4

As for Example 1 except that the dye of Formula 6 was replaced by the dye of the formula:



This dye is C.I. Disperse Orange 1.

In Examples 2-4, the components were incorporated in the amounts shown in Table 1. As in Example 1, the maximum absorption wavelengths ( $\lambda_{\max}$ ) were measured and are given in Table 2. The moulding and irradiation procedures were as described in Example 1, the results being given in Table 2.

### Example 5

97 parts of a compound capable of cationic polymerisation, 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexane carboxylate (hereinafter described as Monomer III), 1 part of a cationic photoinitiator, ( $\eta^6$ -2,4-cyclopentadiene-1-yl) [(1,2,3,4,5,6- $\eta$ )-(1-methylethyl)-benzene]-iron(+1)-hexafluorophosphate (Ciba-Geigy product, CG 24-61) (hereinafter described as Initiator II), and 1 part of the dye of Formula 6 were thoroughly mixed.

The maximum absorption wavelength ( $\lambda_{\max}$ ) and the cure depth were determined as described in Example 1, the results being shown in Table 2.

### Examples 6-8

The procedure described in Example 5 was repeated except that the dye of Formula 6 was replaced, respectively, by the dyes of Formula 7, Formula 8 and Formula 9. The compositions are given in Table 1 and the results, obtained as in Example 1, in Table 2.

### Example 9

A mixture of photoradically curable monomer and photocationically curable monomer together with the appropriate Initiators and sensitiser were used. Thus, as shown in Table 1, 24 parts of Monomer I, 24 parts of Monomer II and 48 parts of Monomer III were thoroughly mixed with 1 part of Initiator I, 1 part of Initiator II, 1 part of Sensitiser I and 1 part of the dye of Formula 6.

The maximum absorption wavelength ( $\lambda_{\max}$ ) and the cure depth were determined as described in Example 1, the results being shown in Table 2.

**Comparative Examples 1-3**

In the Comparative Examples, no dye was added, Monomer I, Monomer II, Initiator I and Sensitizer I being used in Comparative Example 1, Monomer III and Initiator II in Comparative Example 2 and Monomers I, II and III, Initiators I and II and Sensitizer I in Comparative Example 3. The preparation of the photocurable resin compositions and the determination of the maximum absorption wavelength ( $\lambda_{max}$ ) and cure depth were carried out as described in Example 1, the results being shown in Table 2.

It is clear from Table 2 that in Examples 1-9 using dyes having maximum absorption in the wavelength range of the irradiated light, the cure depth was less than 0.5 mm and could be controlled as desired. On the other hand, in Comparative Examples 1-3, the maximum absorption was not in the range 400-600 nm, the main wavelength of the light radiating from the halogen lamp, because no dye was used and the cure depth became 10 mm or more and could not be controlled to the desired low level.

Thus, the invention as hereinbefore described, provides a photopolymerisable resin composition which cures rapidly when exposed to light radiation having a wavelength in the range 450-550 nm to give a cure depth of 0.5 mm or less, said composition being of practical value in photostereolithography applications because of its excellent controllability.

**TABLE 1****Composition of the Photocurable Resin Composition**

Constituent	Example										Comparative		
	Compound	1	2	3	4	5	6	7	8	9	1	2	3
Monomer I		50	50	50	50	-	-	-	-	24	50	-	25
Monomer II		47	47	47	47	-	-	-	-	24	48	-	24
Monomer III		-	-	-	-	97	97	97	97	48	-	98	48
Initiator I		1	1	1	1	-	-	-	-	1	1	-	1
Initiator II		-	-	-	-	1	1	1	1	1	-	1	1
Sensitizer I		1	1	1	1	-	-	-	-	1	1	-	1
Dye													
Formula 6		1	-	-	-	1	-	-	-	1	-	-	-
Formula 7		-	1	-	-	-	1	-	-	-	-	-	-
Formula 8		-	-	1	-	-	-	1	-	-	-	-	-
Formula 9		-	-	-	1	-	-	-	1	-	-	-	-

TABLE 2

Photocurable Resin CompositionMaximum Absorption Wavelength ( $\lambda_{\max}$ ) and Cure Depth (mm)

		( $\lambda_{\max}$ )	Cure depth (mm)
Example	1	509	< 0.1
	2	505	0.2
	3	490	< 0.1
	4	483	0.1
	5	509	0.1
	6	505	0.15
	7	490	< 0.1
	8	483	0.1
	9	509	< 0.1
Comparative Example			
	1	<300	>10.0
	2	<300	>10.0
	3	<300	>10.0

## Claims

1. A method of generating three-dimensional objects comprising applying light of wavelength 450-550 nm by a stereolithographic technique to a photopolymerisable resin composition comprising:
  - (a) a compound having at least one polymerisable unsaturated bond per molecule and a free radical photoinitiator, and/or
  - (b) a compound capable of cationic polymerisation and a cationic photoinitiator,
 said photopolymerisable resin composition also containing a compound of which the wavelength of maximum absorption is in the range 400-600 nm.
2. A method according to claim 1 wherein the compound having a wavelength of maximum absorption in the range 400-600 nm is a dye of the xanthene, anthraquinone or azo series.

3. A method according to claim 1 or claim 2 wherein the photopolymerisable resin composition contains from 0.01 to 10% by weight of the compound having a wavelength of maximum absorption in the range 400-600 nm.

5 4. A method according to claim 3 wherein the photopolymerisable composition contains from 0.01 to 1% by weight of the compound having a wavelength of maximum absorption in the range 400-600 nm.

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European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number

EP 92 30 8452

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 425 440 (CIBA-GEIGY AG) * page 5, line 7 - line 8 * * page 5, line 16 - line 28; claims 1,9,12 *	1-4	G03C9/08 G03F7/031 G03F7/09
A	--- EP-A-0 344 910 (MINNESOTA MINING AND MANUFACTURING COMPANY) * page 8, line 27 - line 33 * * page 14, line 15 - line 17 * * page 14, line 52 * -----	1-4	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G03C G03F C08F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 16 DECEMBER 1992	Examiner DUPART J-M.B.
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>Δ : member of the same patent family, corresponding document</p>			

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# TITLE OF THE INVENTION

PHOTO-CURABLE RESIN COMPOSITION USED FOR PHOTO-  
FABRICATION OF THREE-DIMENSIONAL OBJECTS

## BACKGROUND OF THE INVENTION

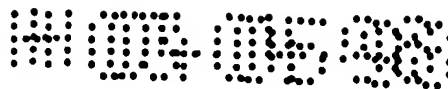
### Field of the Invention

The present invention relates to a photo-curable resin composition used for photo-fabrication of three-dimensional objects.

### Description of the Background Art

In recent years, photo-fabrication processes for forming three-dimensional objects consisting of integrally laminated cured resin layers prepared by repeating a step of forming a cured resin layer by selectively irradiating a liquid photo-curable material with light have been proposed (see Japanese Patent Application Laid-open No. 247515/1985, USP No. 4,575,330 (Japanese Patent Application Laid-open No. 35966/1987), Japanese Patent Application Laid-open No. 101408/1987, Japanese Patent Application Laid-open No. 24119/1993).

A typical example of such a photo-fabrication process comprises forming a curable resin layer having a specified pattern by selectively irradiating with light using, for example, an ultraviolet radiation laser on the surface of a liquid photo-curable material (photo-curable resin composition) in a container, feeding the photo-curable resin



composition equivalent to one layer to form another thin layer of the composition over this cured resin layer, and selectively irradiating this thin layer with light to form a new cured resin layer which is integrally laminated over the previously formed cured resin layer. This step is repeated a number of times, with or without changing the pattern in which the light is irradiated to form a three-dimensional object consisting of integrally laminated multiple cured resin layers. This photo-fabrication process has been attracting considerable attention, because the target three-dimensional object can easily be prepared in a short period of time even if it has a complicated shape.

The following resin compositions (A) to (C) are reported as the photo-curable resin composition used in the photo-fabrication process of three-dimensional objects.

(A) Resin compositions containing a radically polymerizable organic compound such as urethane(meth)acrylate, oligoester(meth)acrylate, epoxy(meth)acrylate, thiol-ene compounds, photosensitive polyimide, and the like (see Japanese Patent Applications Laid-open No. 204915/1989, No. 208305/1990, and No. 160013/1991).

(B) Resin compositions containing a cationically polymerizable organic compound such as an epoxy compound, cyclic ether compound, cyclic lactone compound, cyclic acetal compound, cyclic thioether compound, spiro-orthoester compound, vinyl ether compound, and the like (see Japanese Patent Application Laid-open No. 213304/1989).

The image shows four 4x4 dot patterns arranged horizontally. The first pattern represents the number 1, the second represents 0, the third represents 0, and the fourth represents 5.

Figure 1. The effect of the concentration of the *Agrobacterium* suspension on the transformation efficiency of *Agrobacterium* strains.

Trial	Control	MCI	AD
1	95	85	75
2	95	85	75
3	95	80	70
4	95	78	68
5	95	75	65



#004-005-000

polymerizable compound.

The present invention has been achieved in view of this situation and has an object of providing a photo-curable resin composition used for photo-fabrication, which can be promptly cured to ensure reduction in the period of time required for photo-fabrication processes. Also, the present invention has an object of providing a photocurable composition used for photo-fabrication, which can provide three-dimensional objects which have high toughness and dimensional accuracy.

#### SUMMARY OF THE INVENTION

The above object can be attained in the present invention by a photo-curable resin composition used for photo-fabrication of three-dimensional objects comprising,

- (A) a compound having an oxetane ring,
- (B) a compound having an epoxy group, and
- (C) a cationic photo-initiator.

#### DETAILED DESCRIPTION OF THE INVENTION

##### AND PREFERRED EMBODIMENTS

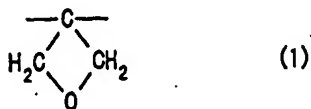
The present invention will now be explained in detail.

##### <(A) Compound having an oxetane ring>

The compound having an oxetane ring (hereinafter may be called from time to time component (A)) contained in the photo-curable resin composition used for photo-fabrication (hereinafter simply called resin composition) of the present invention is a compound having one or more oxetane rings represented by the following formula (1). This compound can be polymerized or crosslinked by irradiation of lights under

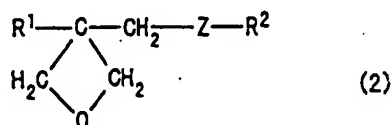
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the presence of a cationic photo-initiator.



As the compounds having an oxetane ring used as component (A), various compounds having one or more oxetane rings may be used as illustrated below.

Examples of the compound having one oxetane ring used as component (A) are the compounds represented by the following formula (2).

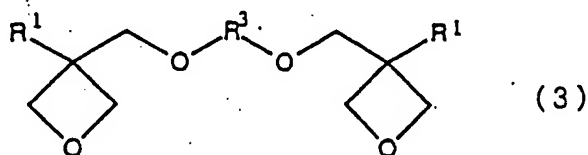


wherein Z represents an oxygen atom or a sulfur atom, R<sup>1</sup> represents a hydrogen atom; fluorine atom; alkyl group having from 1 to 6 carbon atoms such as a methyl group, ethyl group, propyl group, butyl group, or the like; fluoroalkyl group having from 1 to 6 carbon atoms such as a trifluoromethyl group, perfluoroethyl group, perfluoropropyl group, or the like; aryl group having from 6 to 18 carbon atoms such as a phenyl group, naphthyl group, or the like; furyl group, or thienyl group, and R<sup>2</sup> represents a hydrogen atom, alkyl group having from 1 to 6 carbon atoms such as a methyl group, ethyl group, propyl group, butyl group, or the like; alkenyl group having from 2 to 6 carbon atoms such as an 1-propenyl group, 2-propenyl group, 2-

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methyl-1-propenyl group, 2-methyl-2-propenyl group, 1-butenyl group, 2-butenyl group, 3-butenyl group, or the like; aryl group having from 6 to 18 carbon atoms such as a phenyl group, naphthyl group, anthonyl group, phenanthryl group, or the like; aralkyl group having from 7 to 18 carbon atoms which may be either substituted or not, such as benzyl group, fluorobenzyl group, methoxybenzyl group, phenethyl group, styryl group, cinnamyl group, ethoxybenzyl group, or the like; group having other aromatic ring such as an aryloxyalkyl group including a phenoxymethyl group, phenoxyethyl group or the like; alkylcarbonyl group having from 2 to 6 carbon atoms such as an ethylcarbonyl group, propylcarbonyl group, butylcarbonyl group, or the like; alkoxy carbonyl group having from 2 to 6 carbon atoms such as an ethoxycarbonyl group, propoxycarbonyl group, butoxycarbonyl group, or the like; or N-alkylcarbamoyl group having from 2 to 6 carbon atoms such as an ethylcarbamoyl group, propylcarbamoyl group, butylcarbamoyl group, penthylcarbamoyl group, or the like.

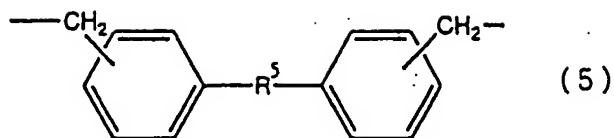
As examples of the compounds having two oxetane rings, the compounds represented by the following formula (3) are given.



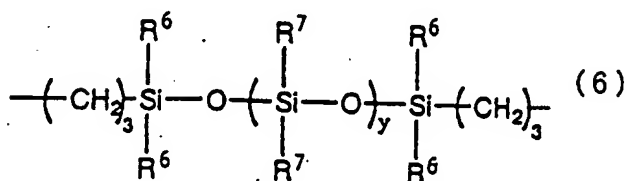
wherein  $R^1$  represents the same group as defined in the formula (2),  $R^3$  represents a linear or branched alkylene group having from 1 to 20 carbon atoms such as an ethylene group, propylene



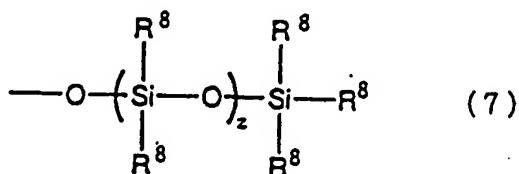
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wherein R<sup>5</sup> represents an oxygen atom, sulfur atom, methylene group, and groups represented by the formulae -NH-, -SO-, -SO<sub>2</sub>-, -C(CF<sub>3</sub>)<sub>2</sub>-, or -C(CH<sub>3</sub>)<sub>2</sub>-.



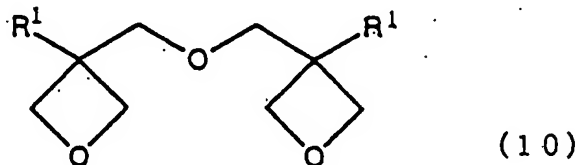
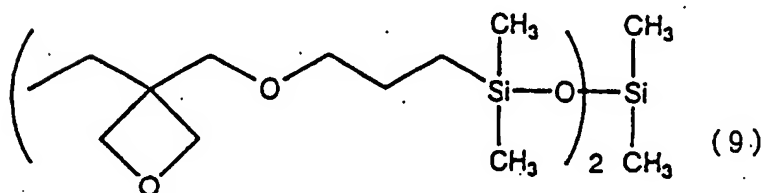
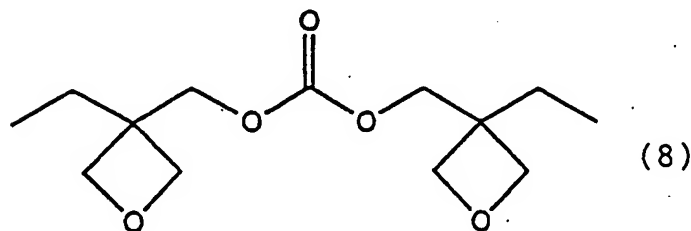
wherein R<sup>6</sup> represents an alkyl group having from 1 to 4 carbon atoms such as a methyl group, ethyl group, propyl group, butyl group, or the like, or aryl group having from 6 to 18 carbon atoms such as a phenyl group, naphthyl group, or the like, y denotes an integer of from 0 to 200, and R<sup>7</sup> represents an alkyl group having from 1 to 4 carbon atoms such as a methyl group, ethyl group, propyl group, butyl group, or the like or aryl group having from 6 to 18 carbon atoms such as a phenyl group, naphthyl group, or the like. Alternatively, R<sup>7</sup> may be a group represented by the following formula (7).



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wherein  $R^9$  represents an alkyl group having from 1 to 4 carbon atoms such as a methyl group, ethyl group, propyl group, butyl group, or the like, or aryl group having from 6 to 18 carbon atoms such as a phenyl group, naphthyl group, or the like, and  $z$  is an integer of from 0 to 100.

Given as examples of the compounds having two oxetane rings are the compounds represented by the following formulas (8)-(10).

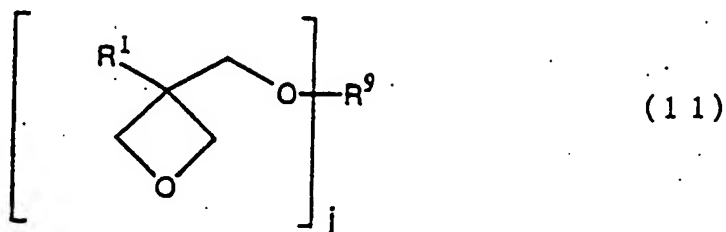


wherein  $R^1$  represents the same group as defined in the formula (2).

As examples of the compound having three or more oxetane

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rings, the compounds represented by the following formula (11) are given.

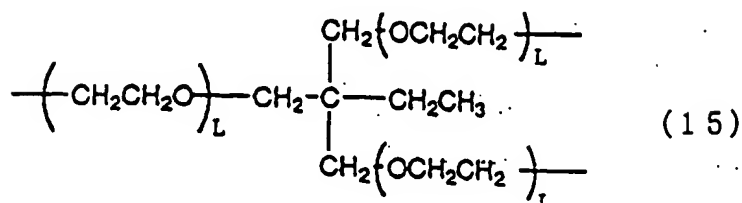
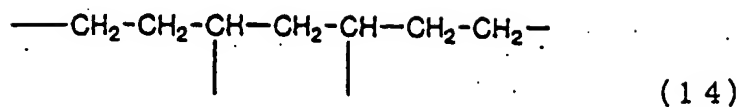
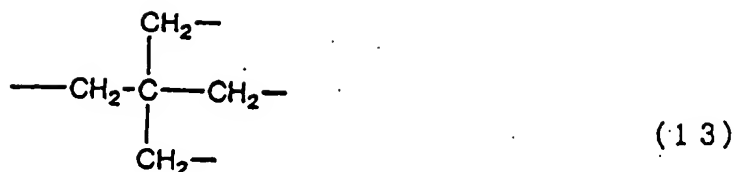


wherein  $R^1$  represents the same group as defined in the formula (2),  $R^9$  represents an organic group with a valence of from 3 to 10; such as linear or branched alkylene groups having from 1 to 30 carbon atoms, for example, the groups represented by the following formulae (12)-(14), linear or branched poly(alkyleneoxy) groups, for example, the groups represented by the following formula (15), or linear or branched polysiloxane containing groups represented by the following formula (16) or (17), and  $j$  denotes an integer of from 3 to 10, equivalent to the valence number of the  $R^9$ .

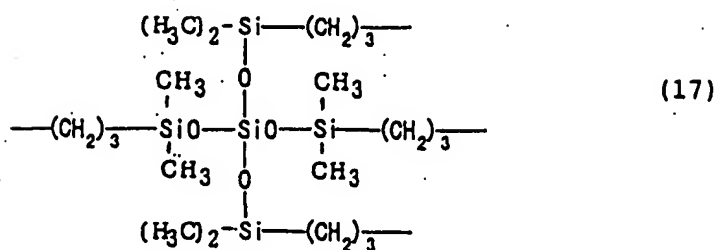
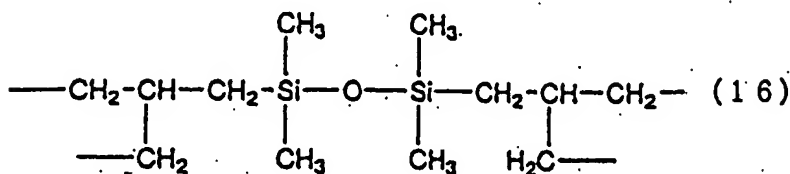


wherein  $R^{10}$  represents an alkyl group having from 1 to 6 carbon atoms such as a methyl group, ethyl group, propyl group, or the like.

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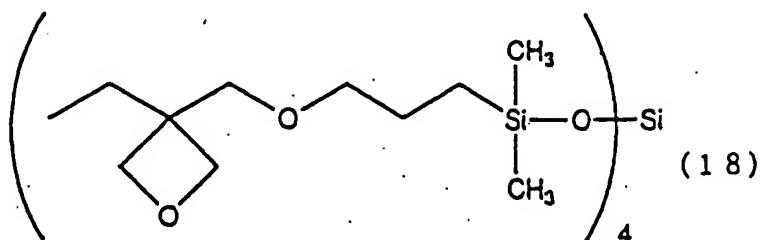


wherein a plurality of Ls, which may be either the same or different, are integers of from 1 to 10.

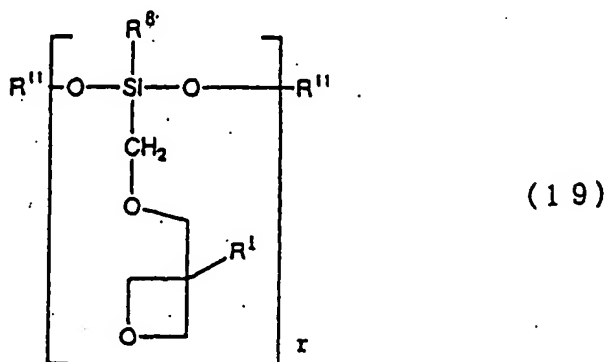


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Also, given as specific examples of the compounds having three or more oxetane rings are the compounds represented by the following formula (18).



The compounds represented by the following formula (19) have from 1 to 10 oxetane rings.



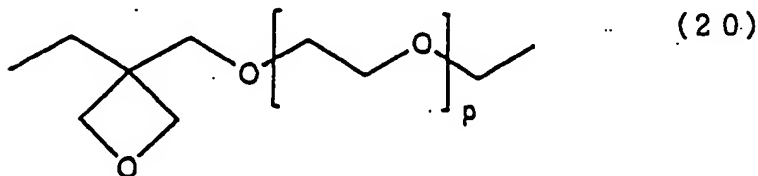
wherein  $R^1$  represents the same group as defined in the formula (2),  $R^8$  represents the same group as defined in the formula (7),  $R''$  represents an alkyl group having from 1 to 4 carbon atoms such as a methyl group, ethyl group, propyl group, butyl group, or the like or a trialkylsilyl group, wherein the alkyl groups may be either the same or different and have from 3 to 12 carbon atoms, such as a trimethylsilyl group, triethylsilyl group, tripropylsilyl group, or tributylsilyl group, and  $z$  is an integer from 1 to 10.

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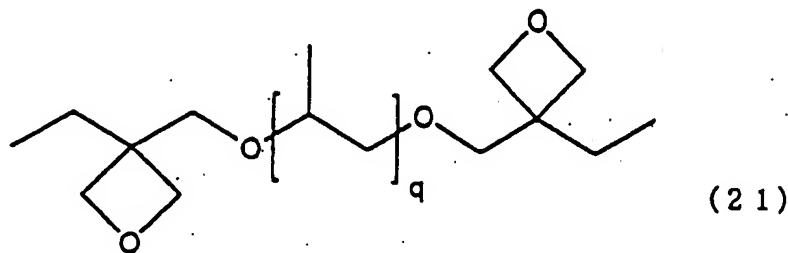
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tripropylsilyl group, or tributylsilyl group, and r is an integer from 1 to 10.

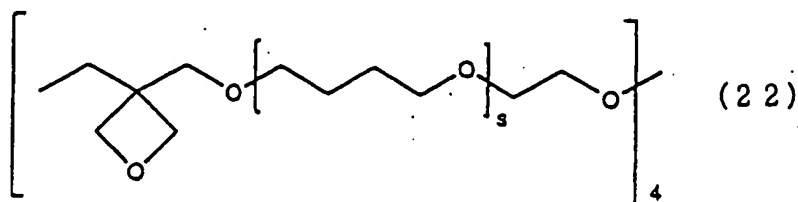
Other than the above examples, the compound having oxetane rings used as component(A) includes compounds with a high molecular weight, e.g. a number average molecular weight reduced polystyrene of 1,000 to 5,000, measured using gel permeation chromatography. Examples of such compounds are the compounds represented by the following formulae (20)-(22).

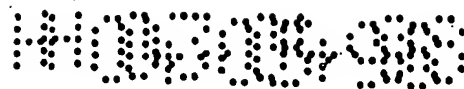


wherein p denotes an integer of from 20 to 200.



wherein q denotes an integer of from 15 to 100.





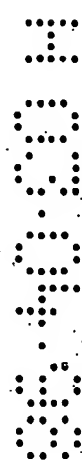
wherein s denotes an integer of from 20 to 200.

Given as specific examples of the compounds having an oxetane ring used as component (A) are the following compounds:

<Compounds having one oxetane ring>

Typical examples of the compounds having one oxetane ring are as follows.

- 3-ethyl-3-hydroxymethyloxetane
- 3-(meth)-allyloxymethyl-3-ethyloxetane
- (3-ethyl-3-oxetanylmethoxy)methylbenzene
- 4-fluoro-[1-(3-ethyl-3-oxetanylmethoxy)methyl]benzene
- 4-methoxy-[1-(3-ethyl-3-oxetanylmethoxy)methyl]benzene
- [1-(3-ethyl-3-oxetanylmethoxy)ethyl]phenyl ether
- isobutoxymethyl(3-ethyl-3-oxetanylmethyl) ether
- isobornyloxyethyl(3-ethyl-3-oxetanylmethyl) ether
- isobornyl(3-ethyl-3-oxetanylmethyl) ether
- 2-ethylhexyl(3-ethyl-3-oxetanylmethyl) ether
- ethyldiethylene glycol (3-ethyl-3-oxetanylmethyl) ether
- dicyclopentadiene (3-ethyl-3-oxetanylmethyl) ether
- dicyclopentenyl(3-ethyl-3-oxetanylmethyl) ether
- dicyclopentenyl(3-ethyl-3-oxetanylmethyl) ether
- tetrahydrofurfuryl(3-ethyl-3-oxetanylmethyl) ether
- tetrabromophenyl(3-ethyl-3-oxetanylmethyl) ether
- 2-tetrabromophenoxyethyl(3-ethyl-3-oxetanylmethyl) ether
- tribromophenyl(3-ethyl-3-oxetanylmethyl) ether
- 2-tribromophenoxyethyl(3-ethyl-3-oxetanylmethyl) ether
- 2-hydroxyethyl(3-ethyl-3-oxetanylmethyl) ether
- 2-hydroxypropyl(3-ethyl-3-oxetanylmethyl) ether



- <Compounds having two or more oxetane rings>

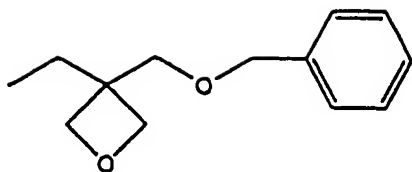
- 3,7-bis(3-oxetanyl)-5-oxa-nonane
- 3,3'-(1,3-(2-methylenyl)propanediylbis(oxymethylene))bis-(3-ethyloxetane)
- 1,4-bis[(3-ethyl-3-oxetanylmethoxy)methyl]benzene
- 1,2-bis[(3-ethyl-3-oxetanylmethoxy)methyl]ethane
- 1,3-bis[(3-ethyl-3-oxetanylmethoxy)methyl]propane
- ethylene glycol bis(3-ethyl-3-oxetanylmethyl) ether
- dicyclopentenylbis(3-ethyl-3-oxetanylmethyl) ether
- triethylene glycol bis(3-ethyl-3-oxetanylmethyl) ether
- tetraethylene glycol bis(3-ethyl-3-oxetanylmethyl) ether
- tricyclodecanediylldimethylene bis(3-ethyl-3-oxetanylmethyl) ether
- trimethylolpropane tris(3-ethyl-3-oxetanylmethyl) ether
- 1,4-bis(3-ethyl-3-oxetanylmethyl)butane
- 1,6-bis(3-ethyl-3-oxetanylmethoxy)hexane
- pentaerythritol tris(3-ethyl-3-oxetanylmethyl) ether
- pentaerythritol tetrakis(3-ethyl-3-oxetanylmethyl) ether
- polyethylene glycol bis(3-ethyl-3-oxetanylmethyl) ether
- dipentaerythritol hexakis(3-ethyl-3-oxetanylmethyl)
- ether, dipentaerythritol pentakis(3-ethyl-3-oxetanylmethyl)

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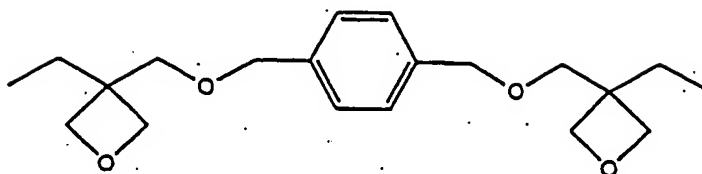
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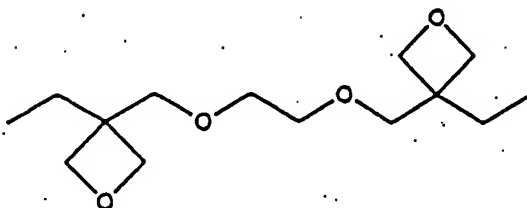
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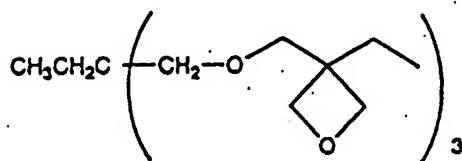
(23)



(24)



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(26)

These compounds having oxetane rings may be used either individually or in combinations of two or more.

The proportion of the component (A) in the resin composition of the present invention is usually 30-97% by weight, preferably 40-96% by weight, and more preferably 50-95% by weight. If the proportion of the component (A) is too low, the rate (curing rate) of the cationic polymerization reaction is so reduced that molding time may be extended and the resolution may tend to be lower. On the other hand, if the

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proportion of the component (A) is too high, there are tendencies that the toughness of the cured product is lower and the rate (curing rate) of the cationic polymerization reaction is reduced.

(B) Compound having an epoxy group

The compound having an epoxy group (hereinafter may be called from time to time component (B)) which is the component of the resin composition of the present invention is a compound having an epoxy group and a number average molecular weight reduced to polystyrene of 1,000-20,000, preferably 1,500-10,000, and more preferably 2,000-5,000, measured using gel permeation chromatography. The molecular weight of these range is preferable to improve the characteristics of the resin composition, such as the viscosity of the resin composition, the period of time required for photo-fabrication, and the toughness of the cured product.

Given as the compounds having an epoxy group are, for example, (1) epoxidated compounds obtained by a process which comprises epoxidating a double bond between carbons of a corresponding compound having an ethylenically unsaturated bond using an appropriate oxidizing agent such as hydrogen peroxide or peroxy acid process (1); (2) polymers having an epoxy group prepared by a process which comprises polymerizing a radically polymerizable monomer containing an epoxy group in a molecule process (2); and (3) compounds having an epoxy group prepared by a known process, e.g. a process comprising reacting a compound having a functional group, e.g. hydroxyl group, with

epichlorohydrin process (3).

In order to prepare compounds having an epoxy group preferably used as the component (B), which have a number average molecular weight reduced to polystyrene of 1,000-20,000, a compound having a number average molecular weight of 1,000-20,000 may be used as the raw material compound having an ethylenically unsaturated bond when using the above process (1). When using the process (2), a known method may be used to prepare a polymer with a desired polymerization degree. Also, when using the process (3), a compound having a number average molecular weight reduced to polystyrene of 1,000-20,000 may be used as the raw material compound having a functional group, e.g. hydroxyl group.

Given as typical examples of the epoxidated compounds of above-mentioned (1) are polymers of conjugated diene monomers, copolymers of conjugated diene monomers and compounds having an ethylenically unsaturated bond, copolymers of diene monomers and compounds having an ethylenically unsaturated bond, and compounds prepared by epoxidating a copolymer such as natural rubber. Illustrating specifically, given as examples of these compounds are compounds produced by epoxidating a polymer of conjugated diene monomers such as a butadiene monomer or isoprene monomer; compounds prepared by epoxidating a copolymer of a conjugated diene monomer and a compound having an ethylenically unsaturated bond, e.g. ethylene, propylene, butene, isobutylene, styrene; compounds prepared by epoxidating a copolymer of a compound having an



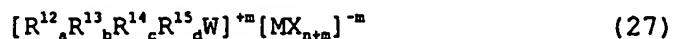
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9  
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The cationic photo-initiator (hereinafter may be called from time to time component (C)) contained in the resin composition of the present invention is a compound capable of generating a molecule initiating cationic polymerization of the components (A) and (B) by receiving radiation such as light.

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Given as especially preferred examples of the cationic photo-initiator are onium salts illustrated by the following formula (27), which are compounds releasing Lewis acid on receiving light:



wherein the cation is an onium ion; W represents S, Se, Te, P, As, Sb, Bi, O, I, Br, Cl, or  $N \equiv N$ ;  $R^{12}$ ,  $R^{13}$ ,  $R^{14}$ , and  $R^{15}$  represent individually the same or different organic group; a, b, c, and d represent individually an integer from 0 to 3, and the provided that  $a+b+c+d$  is equal to the valence number of W. M represents a metal or metalloid which constitutes a center atom of a halide complex. Typical examples of M are B, P, As, Sb, Fe, Sn, Bi, Al, Ca, In, Ti, Zn, Sc, V, Cr, Mn, and Co. X represents a halogen atom such as a fluorine atom, chlorine atom, or bromine atom. m is a substantial electric charge of the halide complex ion and n is the valence of the M.

Given as typical examples of the onium salts represented by the formula (27) are diphenyliodonium, 4-methoxydiphenyliodonium, bis(4-methylphenyl)iodonium, bis(4-tert-butylphenyl)iodonium, bis(dodecylphenyl)iodonium, triphenylsulfonium, diphenyl-4-thiophenoxyphenylsulfonium, bis[4-(diphenylsulfonio)-phenyl]sulfide, bis[4-(di(4-(2-hydroxyethyl)phenyl)sulfonio)-phenyl]sulfide, and  $\eta^5$ -2,4-(cyclopentadienyl)[(1,2,3,4,5,6- $\eta$ )-(methylethyl)-benzene]-iron(1+).

Given as specific examples of the negative ion ( $MX_{n+m}$ ) in

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the above formula (27) are tetrafluoroborate ( $\text{BF}_4^-$ ), hexafluorophosphate ( $\text{PF}_6^-$ ), hexafluoroantimonate ( $\text{SbF}_6^-$ ), hexafluoroarsenate ( $\text{AsF}_6^-$ ), and hexachloroantimonate ( $\text{SbCl}_6^-$ ).

Also, onium salts represented by the general formula  $[\text{MX}_n(\text{OH})^-]$  (wherein M, X, and n are the same as defined in the formula (27)) can be used instead of those represented by the formula  $[\text{MX}_{n+m}]$ . Further, onium salts including a negative ion, for example, perchloric acid ion ( $\text{ClO}_4^-$ ), trifluoromethane sulfonate ion ( $\text{CF}_3\text{SO}_3^-$ ), fluorosulfonate ion ( $\text{FSO}_3^-$ ), toluene sulfonate ion, trinitrobenzene sulfonate negative ion, and trinitrotoluene sulfonate ion, are can be given as other examples of onium salts.

Further, aromatic onium salts can be used as the cationic photo-initiator (C). Among these aromatic onium salts, the following compounds are preferable; aromatic halonium salts described, for example, in Japanese Patent Applications Laid-open No. 151996/1975 and No. 158680/1975; VIA group aromatic onium salts described, for example, in Japanese Patent Applications Laid-open No. 151997/1975, 30899/1977, No. 55420/1981, and No. 125105/1980; VA group aromatic onium salts described, for example, in Japanese Patent Application Laid-open No. 158698/1975; oxosulfoxonium salts described, for example, in Japanese Patent Applications Laid-open No. 8428/1981, No. 149402/1981, and No. 192429/1982; aromatic diazonium salts described, for example, in Japanese Patent Application Laid-open No. 17040/1974; and thiopyrylium salts



described in the specification of USP No. 4,139,655.

Iron/allene complex and aluminium complex/photo-decomposable silica compound initiators are also given as examples of the onium salts.

Given as preferred examples of commercially available products of the cationic photo-initiator which can be used as the component (B) are UVI-6950, UVI-6970 (bis[4-(di(2-hydroxyethyl)phenyl)sulfonio]-phenylsulfide), UVI-6974 (bis[4-diphenylsulfonio)-phenyl]sulfidebis hexafluoroantimonate, UVI-6990 (hexafluorophosphate salt of UVI-6974) (manufactured by Union Carbide Corp), Adekaoptomer SP-151, SP-170 (bis[4-(di(4-(2-hydroxyethyl)phenyl)sulfonio)-phenylsulfide), SP-171 (manufactured by Asahi Denka Kogyo Co., Ltd.), Irgacure 261 ( $\eta^5$ -2,4-(cyclopentadien-1-yl)[(1,2,3,4,5,6- $\eta$ )-(1-methylethyl)benzene]-iron(1+)-hexafluorophosphate(1-)) (manufactured by Ciba Geigy), CI-2481, CI-2624, CI-2639, CI-2064 (manufactured by Nippon Soda Co., Ltd.), CD-1010, CD-1011, CD-1012 (4-(2-hydroxytetradecanyloxy)diphenyliodonium hexafluoroantimonate (manufactured by Sartomer Co., Ltd.), DTS-102, DTS-103, NAT-103, NDS-103 ((4-hydroxynaphthyl)-dimethylsulfonium hexafluoroantimonate), TPS-102 (triphenylsulfonium hexafluoroantimonate), TPS-103 (triphenylsulfonium hexafluoroantimonate), MDS-103 (4-methoxyphenyldiphenylsulfonium hexafluoroantimonate), MPI-103 (4-methoxyphenyliodonium hexafluoroantimonate), BBI-101 (bis(4-tert-butylphenyl)iodonium tetrafluoroborate), BBI-102

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(bis(4-tert-butylphenyl)iodonium hexafluorophosphate), BBI-103 (bis(4-tert-phenyl)iodonium hexafluoroantimonate), (manufactured by Midori Chemical Co., Ltd.), and Degacure K126 (bis[4-(diphenylsulfonio)-phenyl]sulfide bishexafluorophosphate) (manufactured by Degussa Ltd.). Among these, UVI-6970, UVI-6974, Adekaoptomer SP-170, SP-171, CD-1012, MPI-103 are particularly preferable. However, this invention is not limited to these examples.

The above-mentioned cationic photo-initiators can be used as the component (C) either individually or in combinations of two or more.

The proportion of the component (C) in the resin composition of the present invention is 0.1-10% by weight, preferably 0.2-5% by weight, and more preferably 0.3-3% by weight. If the proportion of the component (C) is too low, the photo-curing characteristic of the resin composition obtained is insufficient. No three-dimensional object having sufficient mechanical strength can be produced from such a resin composition. On the other hand, if the proportion of the component (C) is too high, an appropriate light capability (curing depth) cannot be obtained when the resulting resin composition is used in the photo-fabrication process. Mechanical strength such as the toughness of the three-dimensional object prepared from such a resin composition tends to be reduced.

#### <Other components>

In addition to the above essential components (A) to (C),



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bis(3,4-epoxycyclohexanecarboxylate), epoxidated tetrabenzyl alcohol, lactone modified epoxidated tetrahydrobenzyl alcohol, cyclohexene oxide, bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, bisphenol S diglycidyl ether, bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, bisphenol S diglycidyl ether, hydrogenated bisphenol A diglycidyl ether, hydrogenated bisphenol F diglycidyl ether, hydrogenated bisphenol AD diglycidyl ether, brominated bisphenol A diglycidyl ether, brominated bisphenol F diglycidyl ether, brominated bisphenol S diglycidyl ether, an epoxy novolac resin, 1,4-butanediol diglycidyl ether, 1,6-hexanediol diglycidyl ether, glycerol triglycidyl ether, trimethylolpropane triglycidyl ether, polyethylene glycol diglycidyl ether, polypropylene glycol diglycidyl ethers; polyglycidyl ethers of polyether polyol obtained by adding one or more alkylene oxide to aliphatic polyhydric alcohol such as ethylene glycol, propylene glycol, or glycerol; diglycidyl esters of aliphatic long chain dibasic acid; monoglycidyl ethers of aliphatic higher alcohol; monoglycidyl ethers of phenol, cresol, butyl phenol, or polyether alcohol obtained by addition of alkylene oxide to phenol, cresol, or butyl phenol; glycidyl esters of higher fatty acid; epoxidated soybean oil, butyl epoxystearate, octyl epoxystearate, epoxidated polybutadiene, and epoxidated linseed oil.

Other cationically polymerizable compounds which can be additionally used are oxolane such as tetrahydrofuran and 2,3-dimethyltetrahydrofuran; cyclic acetals such as trioxane,

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1,3-dioxolane, and 1,3,6-trioxan cyclooctane; cyclic lactones such as  $\beta$ -propiolactone and  $\epsilon$ -caprolactone; thiiranes such as ethylene sulfide, 1,2-propylene sulfide, and thioepychlorohydrin; thiethanes such as 3,3-dimethyl thiethane; vinyl ethers such as ethylene glycol divinyl ether, triethylene glycol divinyl ether, and trimethylolpropane trivinyl ether; spiro-ortho esters which are obtained by a reaction of epoxy compound and lactone; ethylenically unsaturated compounds such as vinyl cyclohexane, isobutylene, and polybutadiene; and their derivatives.

The resin composition of the present invention may contain polyols for developing photo-curability of the resin composition, and the shape stability (resistance to deformation with time) and characteristic stability (resistance to change in mechanical performance with time) of the three-dimensional object obtained from the resin composition. The polyether polyol has three or more, preferably from 3 to 6 hydroxyl groups in one molecule. If polyether polyols (polyether diols) having less than three hydroxyl groups are used, the object of developing the photo-curing characteristics can not be achieved, and a three-dimensional object with sufficient mechanical strength can not be produced. On the other hand, if polyether polyols having 7 or more hydroxyl groups are used, the elongation and toughness of the three-dimensional object obtained from the resin composition tends to be lower.

Given as specific examples of the polyols are polyether polyols prepared by modifying polyhydric alcohol of more than

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3 valences such as trimethylolpropane, glycerol, pentaerythritol, sorbitol, sucrose, quodorol, or the like by a cyclic ether compound such as ethylene oxide (EO), propylene oxide (PO), butylene oxide, tetrahydrofuran, or the like; caprolactone polyols prepared by modifying using caprolactone; and polyester polyols prepared by modifying using polyester consisting of a dibasic acid and a diol. Specific examples of such polyether polyols are EO modified trimethylolpropane, PO modified trimethylolpropane, tetrahydrofuran modified trimethylolpropane, caprolactone modified trimethylolpropane, EO modified glycerol, PO modified glycerol, tetrahydrofuran modified glycerol, caprolactone modified glycerol, EO modified pentaerythritol, PO modified pentaerythritol, tetrahydrofuran modified pentaerythritol, caprolactone modified pentaerythritol, EO modified sorbitol, PO modified sorbitol, caprolactone modified sorbitol, EO modified sucrose, PO modified sucrose, and EO modified quodor. Among these, EO modified trimethylolpropane, PO modified trimethylolpropane, caprolactone modified trimethylolpropane, PO modified glycerol, caprolactone modified glycerol, and PO modified sorbitol are desirable. However, the present invention is not limited to these examples.

Given as specific examples of commercially available products of the polyols are Sunnix TP-400, Sunnix GP-600, Sunnix GP-1000, Sunnix SP-750, Sunnix GP-250, Sunnix GP-400, Sunnix GP-600 (manufactured by Sanyo Chemical Industries, Ltd.), TMP-3 Glycol, PNT-4 Glycol, EDA-P-4, EDA-P-8 (manufactured by Nippon

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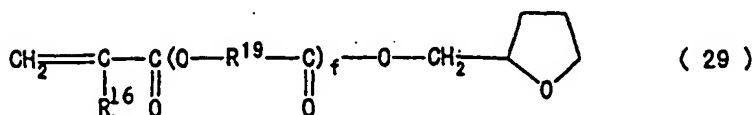
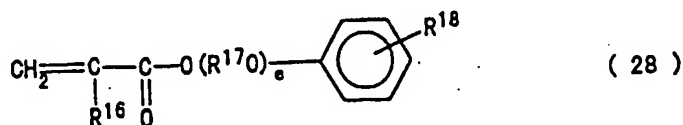
Nyukazai Co., Ltd.), G-300, G-400, G-700, T-400, EDP-450, SP-600, SC-800 (manufactured by Asahi Denka Kogyo Co., Ltd.), TONE 0301, TONE 0305, TONE 0310 (manufactured by Union Carbide Corp.), and PLACCEL 303, PLACCEL 305, PLACCEL 308 (manufactured by Daicel Chemical Industries, Ltd.).

The resin composition of the present invention may include an ethylenically unsaturated monomer which is a radically polymerizable compound to improve the mechanical strength of the cured product and to reduce the time required for fabrication. The ethylenically unsaturated monomer is a compound having ethylenically unsaturated groups (C=C) in the molecule. Given as typical examples of the component (C) are mono-functional monomers having one ethylenically unsaturated bond in one molecule, and polyfunctional monomers having two or more ethylenically unsaturated bonds in one molecule.

Given as examples of the mono-functional monomer are acrylamide, (meth)acryloyl morpholine, 7-amino-3,7-dimethyloctyl (meth)acrylate, isobutoxymethyl (meth)acrylamide, isobornyloxyethyl (meth)acrylate, isobornyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, ethyldiethylene glycol (meth)acrylate, t-octyl (meth)acrylamide, diacetone (meth)acrylamide, dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, lauryl (meth)acrylate, dicyclopentadiene (meth)acrylate, dicyclopentenyl (meth)acrylate, dicyclopentenyl (meth)acrylate, N,N-dimethyl (meth)acrylamide tetrachlorophenyl (meth)acrylate,

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2-tetrachlorophenoxyethyl (meth)acrylate,  
 tetrahydrofurfuryl (meth)acrylate, tetrabromophenyl  
 (meth)acrylate, 2-tetrabromophenoxyethyl (meth)acrylate,  
 2-trichlorophenoxyethyl (meth)acrylate, tribromophenyl  
 (meth)acrylate, 2-tribromophenoxyethyl (meth)acrylate,  
 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl  
 (meth)acrylate, vinyl caprolactam, N-vinyl pyrrolidone,  
 phenoxyethyl (meth)acrylate, butoxyethyl (meth)acrylate,  
 pentachlorophenyl (meth)acrylate, pentabromophenyl  
 (meth)acrylate, polyethylene glycol mono-(meth)acrylate,  
 polypropylene glycol mono-(meth)acrylate, bornyl  
 (meth)acrylate, methyltriethylene diglycol (meth)acrylate,  
 and, the compounds shown in the following general formulas (28)  
 to (30). These compounds may be used either individually or  
 in combinations of two or more.



$$\text{CH}_2=\underset{\text{R}^{16}}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}(\text{O}-\text{R}^{19}-\overset{\text{O}}{\parallel}{\text{C}})_f-\text{O}-\text{CH}_2-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}-\text{CH}\begin{matrix} \nearrow \text{O}-\text{CH}(\text{R}^{16}) \\ \searrow \text{O}-\text{C}(\text{R}^{16})_2 \end{matrix}$$

( 30 )

Given as examples of commercially available products of the monofunctional monomers are Aronix M-101, M-102, M-111, M-113, M-117, M-152, TO-1210 (manufactured by Toagosei Chemical Industry Co., Ltd.), KAYARAD TC-110S, R-564, R-128H (manufactured by Nippon Kayaku Co., Ltd.), and Viscoat 192, Viscoat 220, Viscoat 2311HP, Viscoat 2000, Viscoat 2100, Viscoat 2150, Viscoat 8F, Viscoat 17F (manufactured by Osaka Organic Chemical Industry Co., Ltd.)

Given as preferable examples of the polyfunctional monomers are ethylene glycol di(meth)acrylate, dicyclopentenyl di(meth)acrylate, triethylene glycol diacrylate, tetra

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ethylene glycol di(meth)acrylate, tricyclodecanediyl-  
dimethylene di(meth)acrylate, tris(2-hydroxyethyl)  
isocyanurate di(meth)acrylate, tris(2-hydroxyethyl)  
isocyanurate tri(meth)acrylate, caprolactone modified  
tris(2-hydroxyethyl) isocyanurate tri(meth)acrylate,  
trimethylolpropane tri(meth)acrylate, EO modified  
trimethylolpropane tri(meth)acrylate, PO modified  
trimethylolpropane tri(meth)acrylate, tripropylene glycol  
di(meth)acrylate, neopentyl glycol di(meth)acrylate, both  
terminal (meth)acrylic acid adduct of bisphenol A diglycidyl  
ether, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol  
di(meth)acrylate, pentaerythritol tri(meth)acrylate,  
pentaerythritol tetra(meth)acrylate, polyester  
di(meth)acrylate, polyethylene glycol di(meth)acrylate,  
dipentaerythritol hexa(meth)acrylate, dipentaerythritol  
penta(meth)acrylate, dipentaerythritol tetra(meth)acrylate,  
caprolactone modified dipentaerythritol hexa(meth)acrylate,  
caprolactone modified dipentaerythritol penta(meth)acrylate,  
ditrimethylolpropane tetra(meth)acrylate, EO modified  
bisphenol A di(meth)acrylate, PO modified bisphenol A  
di(meth)acrylate, EO modified hydrogenated bisphenol A  
di(meth)acrylate, PO modified hydrogenated bisphenol A  
di(meth)acrylate, EO modified bisphenol F di(meth)acrylate,  
and phenol novolac polyglycidyl ether. These compounds may be  
used either individually or in combinations of two or more.

These polyfunctional monomer can be selected from the  
above-mentioned tri(meth)acrylate compounds,

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tetra(meth)acrylate compounds, penta(meth)acrylate compounds, and hexa(meth)acrylate compounds. Among these, preferred polyfunctional monomers are trimethylolpropane tri(meth)acrylate, EO modified trimethylolpropane tri(meth)acrylate, PO modified trimethylolpropane tri(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol hexa(meth)acrylate, dipentaerythritol penta(meth)acrylate, dipentaerythritol tetra(meth)acrylate, caprolactone modified dipentaerythritol hexa(meth)acrylate, caprolactone modified dipentaerythritol penta(meth)acrylate, and ditrimethylolpropane tetra(meth)acrylate. However, the present invention is not limited to these examples.

Given as commercially available products of these polyfunctional monomers are SA1002 (manufactured by Mitsubishi Chemical Corp.), Viscoat 195, Viscoat 230, Viscoat 260, Viscoat 215, Viscoat 310, Viscoat 214HP, Viscoat 295, Viscoat 300, Viscoat 360, Viscoat GPT, Viscoat 400, Viscoat 700, Viscoat 540, Viscoat 3000, Viscoat 3700 (manufactured by Osaka Organic Chemical Industry Co., Ltd.), KAYARAD R-526, HDDA, NPGDA, TPGDA, MANDA, R-551, R-712, R-604, R-684, PET-30, GPO-303, TMPTA, THE-330, DPHA, DPHA-2H, DPHA-2C, DPHA-2I, D-310, D-330, DPCA-20, DPCA-30, DPCA-60, DPCA-120, DN-0075, DN-2475, T-1420, T-2020, T-2040, TPA-320, TPA-330, RP-1040, RP-2040, R-011, R-300, R-205 (manufactured by Nippon Kayaku Co., Ltd.), Aronix M-210, M-220, M-233, M-240, M-215, M-305, M-309, M-310, M-315, M-325, M-400, M-6200, M-6400 (manufactured by Toagosei Chemical



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trimethylbenzoyl diphenylphosphine oxides, bis (2,6-dimethoxybenzoyl)-2,4,4-tri-methylpentyl-phosphine oxide, benzyl dimethyl ketal, 1-hydroxycyclohexyl phenyl ketone, 2-hydroxy-2-methyl-1-phenylpropane-1-one, fluorenone, fluorene, benzaldehyde, benzoin ethyl ether, benzoin propyl ether, benzophenone, Michler's ketone, 3-methylacetophenone, 3,3', 4,4'-tetra (t-butyl peroxy-carbonyl) benzophenone (BTTB), and combined compositions of BTTB and xanthene, thioxanthene, cumarin, ketocumarin or other coloring matter photosensitizer. Among these, benzyl dimethyl ketal, 1-hydroxycyclohexyl phenyl ketone, 2,4,6-trimethylbenzoyl diphenylphosphine oxide, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one, and the like are particularly preferred. However, the present invention is not limited to these examples.

Components other than the cationically polymerizable compound and the radical photo-initiator, which may be contained in the resin composition as required, are photosensitizers (polymerization promoters) of amine compounds such as triethanolamine, methyl diethanolamine, triethylamine, diethylamine; photosensitizers including thioxantone or its derivatives, anthraquinone or its derivatives, anthracene or its derivatives, perillene and its derivatives, benzophenone, benzoin isopropylether, and the like; and reaction diluents such as vinyl ether, vinyl sulfide, vinyl urethane, or vinyl urea.

Also, various additives may be incorporated into the resin composition of the present invention. Such additives

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include polymers or oligomers, such as epoxy resin other than the above-mentioned compound having an epoxy group used as the component (B) and other epoxy compounds, polyamide, polyamideimide, polyurethane, polybutadiene, polychloroprene, polyether, polyester, styrene-butadiene-styrene block copolymer, petroleum resin, xylene resin, ketone resin, cellulose resin, fluorine oligomer, silicon oligomer, and polysulfide oligomer; polymerization inhibitors such as phenothiazine or 2,6-di-t-butyl-4-methyl phenol, polymerization initiation adjuvants, age resisters, leveling agents, wettability improvers, surfactants, plasticizers, UV stabilizers, UV absorbers, silane coupling agents, pigments, dyes and the like. Also, the resin composition of the present invention may include inorganic fillers, organic fillers, or the like. Given as specific examples of the above inorganic fillers are solid microparticles of inorganic compounds, such as glass beads, talc microparticles, and silicon oxide, and whiskers of basic magnesium sulfonate, aluminum oxide, or silicon oxide. Specific examples of the above organic fillers are organic solid microparticles of crosslinked polystyrene high polymer, crosslinked polymethacrylate high polymer, crosslinked polyethylene high polymer, and crosslinked polypropylene high polymer. Also, products from such inorganic fillers or organic fillers treated with a silane coupling agent such as aminosilane, epoxysilane, and acrylsilane can be utilized.

<Preparation of Resin composition>

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The resin composition of the present invention can be manufactured by homogeneously blending the above-mentioned components (A) to (C), the optional components which are added as required, and the various additives.

The produced resin compositions are useful for photocurable resin compositions used for photo-fabrication. It is desirable for the photo-curable resin composition of the present invention to possess a viscosity at 25°C in the range of 50-10,000 cps, preferably 100-5,000 cps.

<Photo-fabricating process>

The resin composition of the present invention prepared in this manner is suitable as a photo-curable (liquid) material used in photo-fabrication processes. Specifically, a three-dimensional object with a desired shape can be obtained by using the photo-fabrication process, including selectively irradiating visible light, ultraviolet light, or infrared light on the photo-curable resin composition of the present invention, and feeding the energy required to cure the resin composition.

Various means may be used to selectively irradiate the photo-curable resin composition with light with no specific limitations. Such light irradiation means include, for example, a laser beam, a means for irradiating the composition with light and the like converged by a lens, mirror, or the like, while scanning, a means irradiating the composition with non-convergent light through a mask provided with a fixed pattern through which light is transmitted, and a means for

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irradiating the composition with light via a number of optical fibers bundled in a light conductive member corresponding to a fixed pattern. In the means using a mask, a mask electrooptically produces a mask image consisting of a light transmitting area and non-light-transmitting area according to a prescribed pattern by the same theory as that of the liquid crystal display apparatus. A means using a scanning laser beam with a small spot size is preferred for selectively irradiating the resin composition with light, when a resulting three-dimensional object possesses minute parts or when high dimensional accuracy is required to form the three-dimensional object.

In the above means, the irradiated surface (for example, a plane scanned by light) of the resin composition placed in a vessel is either the liquid surface of the resin composition or the interface of the liquid and a translucent wall of the vessel. When the irradiated surface is the liquid surface or the interface of the liquid and the wall of the vessel, the light can be shone directly out of the vessel or through the vessel.

In the above photo-fabrication process, a desired solid shape can be made by curing fixed parts of the resin composition and then moving the light spot from the cured parts to the uncured parts continuously or stepwise to laminate the cured parts. There are various methods for moving the light spot, for example, a method for moving any of the light source, the vessel for the resin composition, or the cured parts of the resin composition. Also there is a method in which a fresh resin

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composition is supplied to the cured resin composition in the vessel.

Illustrating a typical photo-fabrication process, the surface of a support stage capable of being optionally elevated in the vessel is slightly lowered from the liquid surface to form a thin layer (1) of the resin composition, the thin layer (1) is selectively irradiated with light to form a solid cured resin layer (1'). The resin composition is supplied over this thin layer (1') to form a second thin layer (2), and this thin layer (2) is selectively irradiated with light to laminate a new solid cured resin layer (2') on the thin layer (1'). This step is repeated for a prescribed number of times, with or without changing the pattern subjected to light irradiation, to produce a three-dimensional object consisting of a multiple number of cured resin layers (1') to (n') which are integrally laminated.

The three-dimensional object fabricated in this manner is discharged from the vessel and processed to remove the unreacted photo-curable resin composition remaining on the surface, and washed by a solvent, as required. Given as examples of solvents are an organic solvent which is represented by an alcohol, such as isopropyl alcohol or ethyl alcohol, an organic solvent such as acetone, ethyl acetate, methylethyl ketone, an aliphatic organic solvent such as a terpene, or a low viscosity liquid thermosetting resin or photo-curable resin.

When forming a three-dimensional object with a smooth

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surface, it is desirable that the cured product be washed using the thermosetting resin or photo-curable resin. In this case, it is necessary to post-cure the product by heat emission or light irradiation depending on the type of solvent used in the washing stage. This post-curing treatment is effective not only for curing the resin remaining uncured on the surface of the laminated body, but also for curing the resin composition which remains uncured inside the laminated body. Thus, the post-curing treatment is also effective in the case where the fabricated three-dimensional object is washed with an organic solvent.

The three-dimensional object obtained in this manner has high mechanical strength, high dimensional accuracy, and excellent heat resistance. Also, the three-dimensional object exhibits high stability in maintaining a fixed shape and lasting stable properties. Therefore, the three-dimensional object prepared from the resin composition is preferably used for trial mechanical parts for confirming the functions.

It is desirable to cover the surface of the three-dimensional object by a heat-curable or photo-curable hard coating agent to improve the strength and heat resistance of the surface. As such a hard coating agent, an organic coating agent such as acrylic resin, epoxy resin, silicone resin, or the like, or an inorganic coating agent can be used. These hard coating agents may be used individually or in combinations of two or more.

#### EXAMPLES

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The present invention will be explained in more detail by way of examples, which are not intended to be limiting of the present invention.

<Example 1>

According to the formulation shown in Table 1, 90 parts by weight of (1,4-bis[(3-ethyl-3-oxetanylmethoxy)methyl]-benzene as the component (A), 9 parts by weight of Epolead PB3600 (epoxydated polybutadiene) as the component (B), and 1 part by weight of UVI-6974 (manufactured by Union Carbide Corp.) which was as the component (C) were placed in a vessel equipped with a stirrer and the mixture was reacted with stirring at 60°C for one hour to prepare a transparent liquid composition.

<Examples 2-5>

Transparent liquid compositions were prepared in the same manner as in Example 1 according to the formulations shown in Table 1, except that the different components were used.

<Comparative Examples 1-5>

Transparent liquid compositions (comparative resin compositions) were prepared in the same manner as in Example 1 according to the formulations shown in Table 1, except that the different components and optional components were used. These comparative resin compositions had the following characteristics.

Comparative Example 1: The component (B) was not contained.

Comparative Example 2: 3,4-Epoxycyclohexylmethyl-3',4'-epoxyhexane carboxylate was contained instead of the component (A).

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Comparative Example 3: The component (B) was not contained.

Comparative Example 4: An epoxy/acryl monomer hybrid-type  
photocurable resin composition

Comparative Example 5: Urethane acrylate photocurable resin  
composition.

<Synthesis of urethane acrylate>

3,311 g of isophorone diisocyanate, 10 g of dibutyltin  
dilaurate, and 3 g of 2,6-di(tert)-butyl-4-methylphenol as a  
polymerization inhibitor were placed in a reaction vessel  
equipped with a stirrer. Next, 1,730 g of hydroxyethylacrylate  
was added to the mixture while controlling the temperature at  
less than 20°C. After the addition, the resulting mixture was  
further agitated for one hour. 7,458 g of polyester diol (trade  
mark: P-1010, manufactured by Kuraray Co., Ltd.) which was  
consisting of 3-methyl-1,5-pentane diol and adipic acid and  
which has a number average molecular weight of 1,000 was then  
added to the mixture, keeping the temperature at 40-50°C. The  
reaction was terminated after the agitation was further  
continued for five hours at 50-60°C to obtain urethane acrylate  
(U-1) with a number average molecular weight of 1,680.

<Preparation of liquid resin composition>

36 parts by weight of urethane acrylate (U-1), 18 parts  
by weight of tricyclodecanediyl dimethylene diacrylate as a  
reaction diluent, 23 parts by weight of isobornyl acrylate,  
16 parts by weight of acryloyl morpholine, and 7 parts by weight  
of 1-hydroxyphenyl ketone as a photo-initiator were agitated  
and mixed at 50-60°C to obtain a transparent liquid resin

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composition.

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TABLE 1

	Example					Comparative Example				
	1	2	3	4	5	1	2	3	4	5
Component A • 1,4-bis[(3-ethyl-3-oxetanylmethoxy)methyl]benzene	90	75	70	63	58	99		75		
Component B • Epoxidated polybutadiene (Epolead PB3600)	9	24	9	21	18		24			
Component C • UVI-6974	1	1	1	1	1	1	1	1	1	
• 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate			20				75	24	49	
• 1,4-butanediol diglycidyl ether									21	
• Caprolactone modified trimethylolpropane					8				14	
• Trimethylolpropane triacrylate				14	14				14	
• 1-hydroxyphenyl ketone				1	1				1	7
• Urethane acrylate (U-1)										36
• Tricyctodecanediyl dimethylene diacrylate										18
• Isobornyl acrylate										23
• Acryloyl morpholine										16

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### <Evaluation of the resin composition>

The photo-curable resin compositions prepared in Examples 1-5 and Comparative Examples 1-5 were evaluated by measuring the curability of the resin solution, the toughness of the cured film, and the fabricating capability of three-dimensional objects according to the following methods for evaluation. The results are shown in Table 2.

#### [Curability of the resin solution]

The curability of the resin solution shows a degree (curing rate) of polymerization reaction and crosslinking reaction of the resin composition with respect to the energy of photo-irradiation. The curing rate has influences on the dynamic properties of the cured products, such as Young's modulus, bending elasticity, and the like. Specifically, excellent photo-curability is thought to ensure minimal change in the dynamic properties of the cured product to be produced. In this invention, the curability of the resin solution is evaluated by measuring the Young's modulus of the cured resin film formed by irradiation of lights at different doses.

#### (1) Preparation of test specimens

A coated film with a thickness of 200  $\mu\text{m}$  was prepared by applying a resin composition to a glass plate using an applicator. The surface of the film was irradiated with ultraviolet light at doses of 100  $\text{mJ}/\text{cm}^2$  and 500  $\text{mJ}/\text{cm}^2$  using a conveyor curing apparatus equipped with a metal halide lamp (UB0311-00 type, manufacture by Eye Graphics Co., Ltd.) to prepare a cured resin film. The cured resin film was allowed

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to stand at 23°C and RH 50% in an air conditioned room for one hour to produce test specimens. These test specimens were subjected to the measurement.

(2) Measurement of Young's modulus

The Young's modulus of the test specimens which had been treated at 23°C and RH 50% and cured by irradiation with different doses of lights was measured under the conditions of a drawing rate of 1 mm/min and a bench mark distance of 25 mm using a tension tester (AUTOGRAPH AGS-IKDN, manufactured by Shimazu Corporation).

[Toughness of the cured film]

The toughness of the cured product shows resistance to the external stress. One of the indexes of the toughness is the tensile elongation. In this invention, the toughness of the cured film was evaluated by measuring the tensile elongation of the cured resin film.

(1) Preparation of test specimen

A coated film with a thickness of 200  $\mu\text{m}$  was prepared by applying a resin composition to a glass plate using an applicator. The surface of the film was irradiated with ultraviolet light at a dose of 500  $\text{mJ}/\text{cm}^2$  using a conveyer curing apparatus equipped with a metal halide lamp. The irradiation was terminated before the resin composition was completely cured to prepare a half-cured resin film. Next, the half cured resin film was peeled from the glass plate and placed on releasable paper. The side opposite to that first cured by irradiation was irradiated with ultraviolet light at a dose of

500 mJ/cm<sup>2</sup> to prepare a completely cured resin film.

The cured resin film was allowed to stand at a temperature of 23°C, under a humidity of 50% in air-conditioned room for 24 hours.

(2) Measurement of tensile elongation

The tensile elongation of the test specimen was measured at a temperature of 23°C under a humidity of 50% and the conditions of a drawing rate of 1 mm/min and a bench mark distance of 25 mm using the above tension tester.

[Fabricating capability of three-dimensional objects]

The fabricating capability of the three-dimensional objects was evaluated by measuring the dimensional accuracy of the three-dimensional object prepared from each resin composition and time required for the fabrication.

(1) Fabrication of three-dimensional object

Using an photo-fabrication apparatus (Solid Creator SCS-1000HD, manufactured by Sony Corporation), the resin compositions prepared in the Examples 1-5 and Comparative Examples 1-5 were fabricated according to the following conditions to produce three-dimensional objects each having an H-shape configuration as shown in the front view of Figure 1. With respect to the target dimension of the product, the two columns and the horizontal beam constituting the H figure were all made of a prism with a 6.4 mm x 6.4 mm square cross section. The lengths of the columns and horizontal beam were 44.5 mm and 88.8 mm respectively. Other target dimensions are shown in the Figure.

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The fabricated three-dimensional object was allowed to stand at 23°C and RH 50% in an air-conditioned room to condition.

<Fabricating conditions>

- (i) Laser beam intensity on the liquid surface: 10 mW
- (ii) Scanning velocity: the optimum velocity for the cured depth of the composition to be 0.15 mm.
- (iii) Thickness of cured resin layer: 0.1 mm
- (iv) Number of lamination: 445

(2) Measurement of dimensional accuracy of three-dimensional object

To determine the molding accuracy of the three-dimensional object with the H-shape, the actual widths A to C at positions a to c in the Figure 1 were measured using a calipers having a measuring accuracy of 0.01 mm to calculate the differences between the lengths A and B, and between the lengths C and B according to the equations (I) and (II) illustrated below. The dimensional accuracy was evaluated based on these differences.

$$\text{Dimensional difference between A and B} = (A - B) \quad (\text{I})$$

$$\text{Dimensional difference between C and B} = (C - B) \quad (\text{II})$$

(3) Measurement of the time required for fabrication

The time required for fabricating the three-dimensional object with the H-shape shown in the Figure 1 using the above photo-fabrication apparatus was measured.



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As clear from Table 2, difference in the Young's modulus of cured films prepared from the resin solutions containing the resin compositions of the Examples 1-5 was small when the resin compositions were cured by irradiation with lights at doses of 100 mJ/cm<sup>2</sup> and 500 mJ/cm<sup>2</sup>, demonstrating show excellent curability of the resin composition of the present invention. Also, the Young's modulus of the cured films exceeded 100 kg/mm<sup>2</sup>, indicating that the cured products from these resin compositions exhibit sufficient mechanical strength for photo-fabricating applications. On the other hand, the Young's modulus of the cured film of the resin composition prepared in the Comparative Example 1 excluding the component (B) was so small that no sufficient curability and mechanical strength required for photo-fabricating applications were provided. The resin composition prepared in the Comparative Example 2 excluding the component (A) exhibited only insufficient curability and mechanical strength because the Young's modulus of a cured film of the resin composition was small similarly to that obtained in the Comparative Example 1. The Young's modulus of the photocurable resin composition of the epoxy/acryl monomer hybrid type, which was prepared in the Example 4, was so low that the curability of the resin composition was insufficient for photo-fabricating applications.

The tensile elongation of the cured films prepared from the resin compositions of the Examples 1-5 ranged from 17% to 19%, indicating sufficient toughness for photo-fabricating

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applications. On the other hand, the tensile elongation of the resin compositions excluding the component (B) which were prepared in the Comparative Examples 1 and 3 was 5% and 7% respectively. Therefore, the toughness of the resin compositions excluding the component (B) was insufficient for photo-fabricating applications. In addition, the tensile elongation of the resin composition prepared in the Comparative Example 4 was 6% so that sufficient toughness for photo-fabricating applications could not be provided.

Illustrating the photo-fabricated products of the photocurable resin compositions used for photo-fabrication, which were prepared in the Examples and the Comparative Examples, the photocurable resin compositions prepared in the Examples 1-5 and the urethane acrylate type photocurable resin composition prepared in the comparative Example 5 required less than 10 hours to be optically molded. On the other hand, for the resin composition prepared in the Comparative Example 1, the strength of the resin cured by laser irradiation, which was called "Green strength", was so small that a target three-dimensional object could not be produced. Also, the resin compositions prepared in the Comparative Examples 2 and 4 required more than 20 hours to be optically molded.

Concerning the dimensional accuracy, excellent fabricated products with small dimensional differences could be produced from the resin compositions prepared in the Examples 1-5 and the Comparative Examples of 2 and 4. However, the fabricated products produced from the Comparative Examples 3

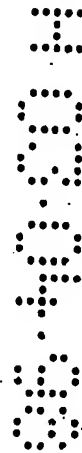
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and 5 exhibited large dimensional differences so that sufficient dimensional accuracy required for photo-fabrication could not be obtained.

As clear from the above illustrations, the photocurable resin composition used for photo-fabrication in the present invention has excellent photocurability, by which the resin composition can be promptly cured by irradiation with lights so that the time required for fabrication can be reduced. Also, shrinkage during curing is so small, so that three-dimensional objects having high dimensional accuracy and excellent mechanical characteristics, especially excellent toughness, can easily be prepared.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a diagram showing the configuration of the three-dimensional object for evaluating the fabricating capability of the resin compositions prepared in the Examples and the Comparative Examples.



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WHAT IS CLAIMED IS:

1. A photocurable resin composition used for photo-fabrication of three-dimensional objects comprising;

- (A) a compound having an oxetane ring,
- (B) a compound having an epoxy group, and
- (C) a cationic photo-initiator.

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#### ABSTRACT OF THE DISCLOSURE

A photocurable resin composition suitable for photo-fabrication. The resin composition capable of being promptly cured by photo-irradiation, thereby reducing fabricating time and providing cured products having excellent mechanical strength and minimized shrinkage during curing to ensure high dimensional accuracy. The composition comprises (A) a compound having an oxetane ring, (B) a compound having an epoxy group, and (C) a cationic photo-initiator.

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